

Magnetic Feshbach resonances in collisions of closed-shell $^1\Sigma$ molecules

Alisdair O. G. Wallis and Roman V. Krems

*Department of Chemistry, University of British Columbia,
Vancouver, British Columbia, V6T 1Z1, Canada*

(Dated: September 10, 2012)

Magnetic Feshbach resonances play a central role in experimental research of atomic gases at ultracold temperatures. A major thrust of current research is to create an ultracold gas of diatomic alkali-metal molecules in the ground rovibrational state of the ground electronic $^1\Sigma$ state. Can ultracold $^1\Sigma$ molecules be controlled by means of magnetic Feshbach resonances? Unlike alkali metal atoms, $^1\Sigma$ diatomic molecules have no unpaired electrons. The response of $^1\Sigma$ molecules to an external magnetic field is determined by the spin structure of the atomic nuclei. We present quantum scattering calculations illustrating that nuclear spin relaxation and Feshbach resonances in ultracold molecule-molecule collisions for $^1\Sigma$ molecules in a magnetic field are highly probable. We show that certain Zeeman states of $^1\Sigma$ molecules exhibit broad resonances and weak inelastic scattering, which makes these states ideal for experiments exploiting magnetic field control of ultracold molecular gases.

PACS numbers:

Much of the success of experimental research with ultracold atomic gases is due to the possibility of tuning the scattering length of ultracold alkali metal atoms by means of magnetic Feshbach resonances [1]. The scattering length near a Feshbach resonance undergoes rapid variation as a function of the magnetic field, which has been used for experimental studies of Bose–Einstein condensation (BEC) [2, 3], bosonic superfluidity [4], quantum magnetism [5], many-body spin dynamics [6], Efimov states [7], Bardeen–Cooper–Schrieffer (BCS) superfluidity [8] and the BEC–BCS crossover [9, 10]. A major thrust of current experimental work is to extend this work to ultracold molecules [11]. Of particular interest are polar alkali metal dimers in the ground $^1\Sigma$ electronic state produced by photoassociation of ultracold atoms. Several experiments have recently demonstrated the creation of ultracold alkali metal dimers KRb [12] in the ro-vibrational ground state of the electronic ground state and rapid progress is being made with RbCs [13, 14].

Polar molecules offer long-range dipolar interactions, which can be used for new exciting applications such as the study of dipolar crystals [15] and ultracold controlled chemistry [16, 17]. While the long-range interactions between polar molecules can be controlled by an external electric field [18, 19], many applications, such as quantum simulation of spin-lattice models [20] or the study of dipolar effects on BEC and the BEC - BCS cross-over [21], require independent control over short-range and long-range interactions. The short-range interactions could, in principle, be controlled by magnetic Feshbach resonances. However, unlike alkali metal atoms, $^1\Sigma$ molecules have no unpaired electrons and it is currently believed that the binary interactions between $^1\Sigma$ molecules cannot be controlled by a magnetic field.

For two interaction partners A and B , a magnetic Feshbach resonance occurs when a bound state of the AB

complex has a different magnetic moment from that of the isolated particles so that the energy of the bound state can be tuned across an $A + B$ collision threshold by varying an external magnetic field. The width of the resonance is proportional to the coupling between the bound and continuum states. For collisions of two alkali-metal atoms in the ground electronic state 2S , these couplings are determined by the energy difference between the singlet ($^1\Sigma$) and triplet ($^3\Sigma$) electronic states of the collision complex and strong hyperfine interactions between the unpaired electron spin and the nuclear spin [1]. Because $^1\Sigma$ molecules have a closed electronic shell, the interaction properties of two $^1\Sigma$ molecules are determined by a single potential energy surface. The response of $^1\Sigma$ molecules to an external magnetic field is determined by the magnetic moments of the nuclei. The nuclear spin states of atoms or molecules with closed electronic shells are generally well protected from the effects of collision dynamics. However, we show in the present work that a subtle interplay of couplings induced by the molecule - molecule interaction potential and the interactions induced by molecular rotations gives rise to magnetic Feshbach resonances that can be used to control ultracold collisions of $^1\Sigma$ molecules.

Figure 1 shows the Zeeman energy levels of the $^{87}\text{Rb}^{133}\text{Cs}(X^1\Sigma^+)$ molecule in the ground rotational state. At zero magnetic field, the energy levels are labeled by the quantum number F of the total angular momentum including the nuclear spins. At high magnetic fields, the energy levels can be labeled by the quantum numbers M_{Rb} and M_{Cs} specifying the projections of the nuclear spins of Rb and Cs on the magnetic field axis. Recent experiments demonstrated that ultracold alkali metal dimers can be selectively prepared in any Zeeman level of the ground rotational state [22]. In the present work, we examine the strength of collision-induced couplings between the Zeeman states shown in

Figure 1. These couplings lead to nuclear spin relaxation and magnetic Feshbach resonances in molecule - molecule collisions. As follows from the equations presented below, if two $^1\Sigma$ molecules were initially prepared and remained during a collision in the rotational ground state with $N = 0$, the nuclear spin states would have been completely decoupled from translational motion of the molecules. However, the molecule - molecule interaction potential induces couplings between rotational states that modify the hyperfine interactions during collisions. These couplings may give rise to magnetic Feshbach resonances and induce the nuclear spin relaxation in molecule - molecule collisions.

In order to calculate the energy levels shown in Figure 1, we diagonalize the following Hamiltonian [23]:

$$\hat{H} = B\hat{N}^2 + \hat{H}_{\text{hf}} + \hat{H}_{\text{Zeeman}}, \quad (1)$$

where \hat{N} is the molecular angular momentum excluding nuclear spins and \hat{H}_{hf} is the hyperfine Hamiltonian [24],

$$\hat{H}_{\text{hf}} = \sum_{i=1}^2 \mathbf{V}_i \cdot \mathbf{Q}_i + \sum_{i=1}^2 c_i \mathbf{N} \cdot \mathbf{I}_i + c_3 \mathbf{I}_1 \cdot \mathbf{T} \cdot \mathbf{I}_2 + c_4 \mathbf{I}_1 \cdot \mathbf{I}_2, \quad (2)$$

where \mathbf{I}_i is the nuclear spin of nucleus i . The first term in the hyperfine Hamiltonian is the electric-quadrupole interaction, which represents the interaction of the nuclear quadrupole moment \mathbf{Q}_i with the electric field gradient \mathbf{V}_i at nucleus i . The second term is the nuclear spin-rotation interaction between the magnetic moment of the nuclear spin and the magnetic moment created by the molecular rotation. The third and fourth terms describe the tensor and scalar parts of the nuclear spin-spin interaction, respectively [25]. The interaction with the magnetic field is described by

$$\hat{H}_{\text{Zeeman}} = -g_r \mu_N \mathbf{N} \cdot \mathbf{B} - \sum_{i=1}^2 g_i \mu_N \mathbf{I}_i \cdot \mathbf{B} (1 - \sigma_i), \quad (3)$$

which consists of rotational and nuclear contributions respectively, where g_r and g_i are the rotational and nuclear g -factors and σ_i is a nuclear screening factor. The constants c_i have been calculated by Aldegunde *et al.* [24]. We use the fully uncoupled space-fixed basis, $|I_{\text{Rb}} M_{\text{Rb}} \rangle |I_{\text{Cs}} M_{\text{Cs}} \rangle |N M_N \rangle$, where $I_{s^7\text{Rb}} = \frac{3}{2}$, $I_{133\text{Cs}} = \frac{7}{2}$ and the projections of the corresponding angular momenta are defined with respect to the z -axis directed along the magnetic field vector.

To evaluate the outcome of collisions, we follow the approach described in Refs. [26, 27]. The total scattering wavefunction, for molecules A and B , is expanded in the uncoupled space-fixed basis $|\tau_A \tau_B L M_L \rangle$, where $|\tau_i \rangle = |I_{\text{Rb}}^{(i)} M_{\text{Rb}}^{(i)} I_{\text{Cs}}^{(i)} M_{\text{Cs}}^{(i)} N^{(i)} M_N^{(i)} \rangle$, for molecule i , and L is the end-over-end angular momentum of the molecule - molecule collision complex. This basis is then symmetrized with respect to the interchange of two identical

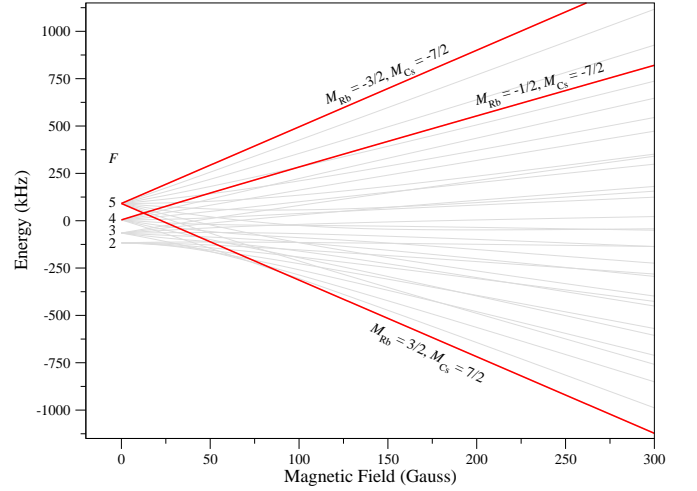


FIG. 1: (color online) The hyperfine structure of the $^{87}\text{Rb}^{133}\text{Cs}(X^1\Sigma^+)$ rotational ground-state. The hyperfine states considered here are highlighted in red.

molecules [28, 29]. In a magnetic field, the total angular momentum projection M_{tot} and the parity are conserved and the Hamiltonian can be block diagonalized. For each given M_{tot} and parity, sets of coupled-channel equations are constructed, solutions to which are propagated outwards over a radial grid of molecule - molecule separation, using the improved log-derivative method of Manolopoulos [30]. The radial grid was divided into short (4 to 80 a_0) and long range (80 to 1000 a_0) regions, with grid step sizes of 0.0305 and 1 a_0 respectively. At 1000 a_0 , the log-derivative matrix is transformed into the basis of asymptotic eigenvectors and matched to the appropriate scattering boundary conditions [31] to obtain the S -matrix. The scattering cross sections are calculated from the S -matrix elements [26].

The dimension of the two-molecule basis set grows very fast as the number of the rotational states N and the orbital angular momentum states L is increased. The majority of the calculations presented here are performed with the basis set including three rotational states $N \leq 2$ for each molecule and all $L \leq 2$ states. While this basis set does not yield fully converged results, it is large enough to encapsulate the essential physics of molecule-molecule interactions [32]. In addition, we examined carefully the basis set dependence of our results. The calculations were carried out for $M_{\text{tot}} = \pm 10$ and ± 8 , yielding 976 and 3129 coupled differential equations respectively.

There is currently no full potential energy surface available for the $\text{RbCs}(X^1\Sigma^+)$ - $\text{RbCs}(X^1\Sigma^+)$ molecular system. We use the potential surface computed for $\text{NH}(^3\Sigma^-)$ - $\text{NH}(^3\Sigma^-)$ collisions by Janssen *et al.* [33]. In order to examine the potential surface dependence and present results relevant for the RbCs - RbCs system, we scale the NH - NH potential surface and compute the

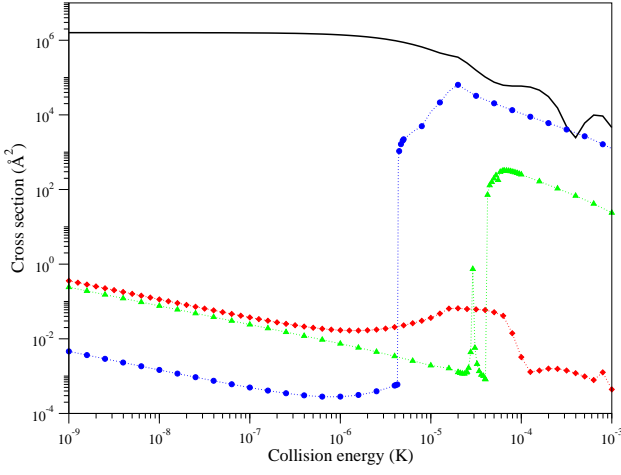


FIG. 2: (color online) s -wave elastic and hyperfine relaxation cross sections as a function of the collision energy. For two molecules in the initial ($M_{\text{Rb}} = -\frac{3}{2}, M_{\text{Cs}} = -\frac{7}{2}$) state the elastic (black-solid) and hyperfine relaxation (red-diamonds) cross sections are shown at a magnetic field of 10 Gauss. For two molecules in the initial ($M_{\text{Rb}} = -\frac{1}{2}, M_{\text{Cs}} = -\frac{7}{2}$) state, the relaxation cross section is shown for magnetic fields of 10 (blue-circles) and 1000 (green-triangles) Gauss; the elastic cross section is very similar to the ($M_{\text{Rb}} = -\frac{3}{2}, M_{\text{Cs}} = -\frac{7}{2}$) elastic cross section and is not shown.

results in a wide range of the scaling parameters.

We begin by analyzing the probability of nuclear spin relaxation of two molecules initially prepared in the maximally spin-stretched state, labeled in Figure 1 as ($M_{\text{Rb}} = -3/2, M_{\text{Cs}} = -7/2$), and two molecules prepared in a lower energy state ($M_{\text{Rb}} = -1/2, M_{\text{Cs}} = -7/2$). Figure 2 shows the results of the scattering calculations, illustrating two striking observations. First, the cross sections for nuclear spin relaxation have a large magnitude and can, for the initial state ($M_{\text{Rb}} = -1/2, M_{\text{Cs}} = -7/2$) be comparable with the cross sections for elastic scattering. Second, the cross sections for the inelastic relaxation from the ($M_{\text{Rb}} = -1/2, M_{\text{Cs}} = -7/2$) state undergo a rapid increase at a certain collision energy, marking the opening of a barrierless collision channel. Below this collision energy all relaxation channels contain a d -wave barrier. This illustrates that there are significant couplings between the nuclear spin states. For collisions between molecules in the ($M_{\text{Rb}} = -3/2, M_{\text{Cs}} = -7/2$) state, the predominant coupling responsible for Feshbach resonances is the second order interplay of the nuclear quadrupole and potential interactions. For molecules in the ($M_{\text{Rb}} = -1/2, M_{\text{Cs}} = -7/2$) state and in other non-stretched states an additional first order scalar spin-spin coupling also contributes.

The same couplings give rise to magnetic Feshbach resonances. In order to illustrate this, we compute the elastic and inelastic scattering cross sections for molecules prepared in the state ($M_{\text{Rb}} = -1/2, M_{\text{Cs}} = -7/2$) as functions of the magnetic field. Figure 3 demonstrates

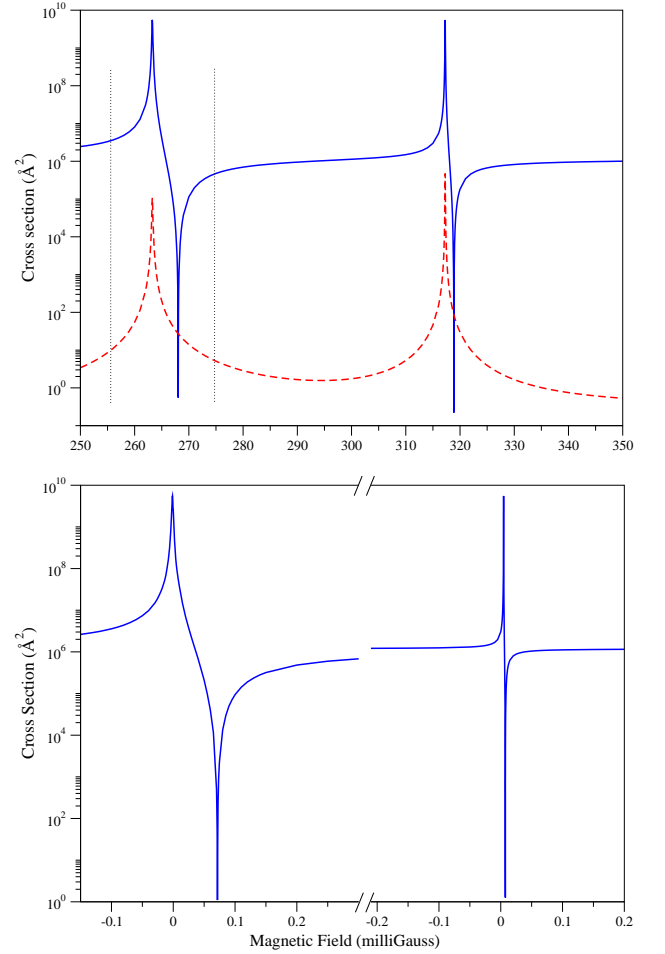


FIG. 3: (color online) Magnetic Feshbach resonances in molecule-molecule collisions computed using the $N \leq 2, L \leq 2$ basis set at collision energy of 1 nK. Upper panel: magnetic Feshbach resonances for two molecules in low-field seeking ($M_{\text{Rb}} = -\frac{1}{2}, M_{\text{Cs}} = -\frac{7}{2}$) state. Lower panel: two magnetic Feshbach resonances for two molecules in the ($M_{\text{Rb}} = \frac{3}{2}, M_{\text{Cs}} = \frac{7}{2}$) absolute ground state, at 1210.1 and 1670.2 Gauss.

that the cross sections exhibit the resonant variation over the magnetic field interval as wide as ~ 10 Gauss. The inelastic cross sections remain generally much smaller than the elastic cross section, as long as the collision energy is low enough (to the left of the enhancement point in Figure 2).

The absolute ground state of RbCs, labeled in Figure 1 as ($M_{\text{Rb}} = 3/2, M_{\text{Cs}} = 7/2$) is particularly interesting for applications that need to avoid inelastic collisions. Figure 3 illustrates that molecules prepared in this state exhibit Feshbach resonances that affect the scattering cross sections over an interval of 0.1 mGauss. For collisions between molecules in the absolute ground state, the couplings are the same as for the ($M_{\text{Rb}} = -3/2, M_{\text{Cs}} = -7/2$) state.

The quantitative accuracy of the results presented is

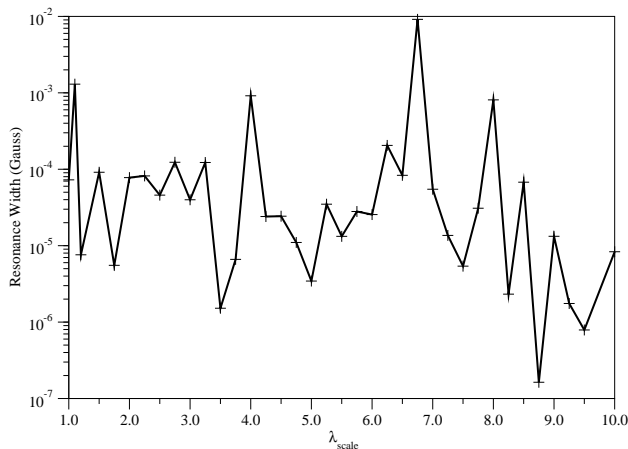


FIG. 4: (color online) For two molecules in the absolute ground state ($M_{\text{Rb}} = \frac{3}{2}$, $M_{\text{Cs}} = \frac{7}{2}$), the width of the largest Feshbach resonance in the range of magnetic fields from 0 to 4000 Gauss is shown as a function of the interaction potential.

limited by the interaction potential surface and the basis set restrictions. While it is unlikely that increasing the basis set may decrease the resonance widths observed, it is necessary to confirm this. To perform calculations using larger basis sets, approximations are required to make the calculations feasible. The highest order off-diagonal coupling, that is predominantly responsible for Feshbach resonances, is the second order interplay of the nuclear quadrupole and potential interactions. To a first approximation we can neglect all states that are not coupled to a desired initial channel via this second order coupling. Practically this requires neglecting channels that differ from the initial channel by $|\Delta M_{I_{\text{tot}}}| > 2N_{\text{max}}$, where $M_{I_{\text{tot}}} = M_{\text{Rb}}^{(A)} + M_{\text{Cs}}^{(A)} + M_{\text{Rb}}^{(B)} + M_{\text{Cs}}^{(B)}$ and N_{max} is the largest value of the rotational angular momentum included in the calculation. Neglecting these states approximately halves the number of channels in the calculation while only introducing a 1% error in the calculated cross sections.

Using this approximation, we can incorporate additional basis states. For molecules in the absolute ground state, increasing the number of partial waves from $L \leq 2$ to $L \leq 4$ triples the number of Feshbach resonances to approximately three resonances per 1000 Gauss. While most of these additional resonances are very narrow, there is always at least one resonance per 1000 Gauss with the width > 0.1 milliGauss. Increasing the number of rotational states from three to four ($N \leq 3$) rotational states per molecule, does not affect the resonance density but increases the resonance widths by up to a factor of approximately thirty. Our predictions regarding the widths of the resonances should thus be considered as *lower* bounds.

To demonstrate the effect of interaction potential variation on the width of the resonances, we scale the NH-

NH potential by a linear factor, $V^{\text{scaled}} = \lambda_{\text{scale}} V^{\text{original}}$. Figure 4 displays the width of the widest resonance for molecules in the absolute ground state in the magnetic field range between 0 and 4000 Gauss as a function of the potential scaling factor, using the above approximation with three rotational states per molecule and $L \leq 2$. The resonance width oscillates between 10^{-7} Gauss and 10^{-2} Gauss, with an average of 3.6×10^{-4} Gauss. As the potential is varied the larger resonances are moved out of the magnetic field region considered, and thus for the smaller values in figure 4 a larger resonance could be found by considering a larger range of magnetic field.

In summary, we have presented a rigorous analysis of the effects of magnetic fields on collisions of $^1\Sigma$ molecules. We showed that the interaction of the nuclear spins with the magnetic field gives rise to magnetic Feshbach resonances mediated by an interplay of hyperfine interactions and the electronic interaction potential between molecules. Our calculations show that $^1\Sigma$ molecules prepared in the absolute ground state may exhibit magnetic Feshbach resonances with widths > 1 milliGauss. Molecules prepared in excited Zeeman levels of the rovibrationally ground state may exhibit even broader resonances, with widths > 1 Gauss. Although excited Zeeman levels are subject to inelastic Zeeman relaxation changing the nuclear spin projections, we found that certain states exhibit broad Feshbach resonances and suppressed inelastic relaxation. These states appear to be ideal for experiments exploiting the magnetic field control of intermolecular interactions. These states exhibit the unusual dynamics of inelastic collisions that is extremely sensitive to the opening of excited collision thresholds, which can be used as a new mechanism for controlling binary molecule interactions.

This work was supported by NSERC of Canada

-
- [1] C. Chin, R. Grimm, P. Julienne, and E. Tiesinga, Rev. Mod. Phys. **82**, 1225 (2010).
 - [2] S. Inouye, M. R. Andrews, J. Stenger, H. J. Miesner, D. M. Stamper-Kurn, and W. Ketterle, Nature **392**, 151 (1998).
 - [3] E. Timmermans, P. Tommasini, M. Hussein, and A. Kerman, Phys. Rep. **315**, 199 (1999).
 - [4] K. Sengupta and N. Dupuis, Europhys. Lett. **70**, 586 (2005).
 - [5] L.-M. Duan, E. Demler, and M. D. Lukin, Phys. Rev. Lett. **91**, 090402 (2003).
 - [6] A. Widera, S. Trotzky, P. Cheinet, S. Fölling, F. Gerbier, I. Bloch, V. Gritsev, M. D. Lukin, and E. Demler, Phys. Rev. Lett. **100**, 140401 (2008).
 - [7] T. Kraemer, M. Mark, P. Waldburger, J. G. Danzl, C. Chin, B. Engeser, A. D. Lange, K. Pilch, A. Jaakkola, H. C. Nägerl, et al., Nature **440**, 315 (2006).
 - [8] J. Kinast, S. L. Hemmer, M. E. Gehm, A. Turlapov, and J. E. Thomas, Phys. Rev. Lett. **92**, 150402 (2004).

- [9] C. A. Regal, M. Greiner, and D. S. Jin, Phys. Rev. Lett. **92**, 040403 (2004).
- [10] T. Bourdel, L. Khaykovich, J. Cubizolles, J. Zhang, F. Chevy, M. Teichmann, L. Tarruell, S. J. J. M. F. Kokkelmans, and C. Salomon, Phys. Rev. Lett. **93**, 050401 (2004).
- [11] R. V. Krems, W. C. Stwalley, and B. Friedrich, *Cold Molecules: Theory, Experiment, Applications* (CRC Press, Boca Raton, 2009).
- [12] K.-K. Ni, S. Ospelkaus, M. H. G. de Miranda, A. Pe'er, B. Neyenhuis, J. J. Zirbel, S. Kotochigova, P. S. Julienne, D. S. Jin, and J. Ye, Science **322**, 231 (2008).
- [13] H. W. Cho, D. J. McCarron, D. L. Jenkin, M. P. Köppinger, and S. L. Cornish, Eur. Phys. J. D **65**, 125 (2011).
- [14] T. Takekoshi, M. Debatin, R. Rameshan, F. Ferlaino, R. Grimm, H. Nägerl, C. Sauer, J. Hutson, P. Julienne, S. Kotochigova, et al., Phys. Rev. A **85**, 032506 (2012).
- [15] G. Pupillo, A. Micheli, H. Büchler, and P. Zoller, in *Cold Molecules: Theory, Experiment, Applications* (CRC Press, Boca Raton, 2009), pp. 421–469.
- [16] R. V. Krems, Phys. Chem. Chem. Phys. **10**, 4079 (2008).
- [17] S. Ospelkaus, K. Ni, D. Wang, M. De Miranda, B. Neyenhuis, G. Quémener, P. Julienne, J. L. Bohn, D. Jin, and J. Ye, Science **327**, 853 (2010).
- [18] K. Ni, S. Ospelkaus, D. Wang, G. Quémener, B. Neyenhuis, M. De Miranda, J. L. Bohn, J. Ye, and D. Jin, Nature **464**, 1324 (2010).
- [19] G. Quémener and J. L. Bohn, Phys. Rev. A **81**, 022702 (2010).
- [20] A. Micheli, G. K. Brennen, and P. Zoller, Nature Physics **2**, 341 (2006).
- [21] M. Baranov, L. Dobrek, K. Góral, L. Santos, and M. Lewenstein, Phys. Scr. **102**, 74 (2002).
- [22] S. Ospelkaus, K.-K. Ni, G. Quémener, B. Neyenhuis, D. Wang, M. H. G. de Miranda, J. L. Bohn, J. Ye, and D. S. Jin, Phys. Rev. Lett. **104**, 030402 (2010).
- [23] J. M. Brown and A. Carrington, *Rotational Spectroscopy of Diatomic Molecules* (Cambridge University Press, Cambridge, 2003).
- [24] J. Aldegunde, B. A. Rivington, P. S. Żuchowski, and J. M. Hutson, Phys. Rev. A **78**, 033434 (2008).
- [25] D. L. Bryce and R. E. Wasylshen, Acc. Chem. Res. **36**, 327 (2003).
- [26] R. V. Krems and A. Dalgarno, J. Chem. Phys. **120**, 2296 (2004).
- [27] T. V. Tscherbul, Y. V. Suleimanov, V. Aquilanti, and R. V. Krems, New J. Phys. **11**, 055021 (2009).
- [28] S. Green, J. Chem. Phys. **62**, 2271 (1975).
- [29] M. Alexander and A. E. DePristo, J. Chem. Phys. **66**, 2166 (1977).
- [30] D. E. Manolopoulos, J. Chem. Phys. **85**, 6425 (1986).
- [31] B. R. Johnson, J. Comput. Phys. **13**, 445 (1973).
- [32] L. M. C. Janssen, P. S. Żuchowski, A. van der Avoird, G. C. Groenenboom, and J. M. Hutson, Phys. Rev. A **83**, 022713 (2011).
- [33] L. M. C. Janssen, G. C. Groenenboom, A. Van Der Avoird, P. S. Żuchowski, and R. Podeszwa, J. Chem. Phys. **131**, 224314 (2009).